



Effect of Pt/Pd ratio on catalytic activity and redox behavior of bimetallic Pt–Pd/Al₂O₃ catalysts for CH₄ combustion

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ABSTRACT

In the present work CH₄ combustion activity and reduction/oxidation behavior of bimetallic Pt–Pd/Al₂O₃ catalysts with constant Pd loading (2%, w/w) and different Pt/Pd atomic ratios (0, 0.10, 0.25 and 1) are investigated in the presence of alternated CH₄ lean combustion/CH₄-reducing pulses at 350 °C. In the fresh samples, according to XRD and CH₄-TPR measurements, Pd is always totally present as PdO and the CH₄ combustion activity is progressively promoted by Pt addition. On the other hand the reactivity scale is substantially changed (Pt/Pd = 0.10 ≥ Pt/Pd = 0 > Pt/Pd = 0.25 ≫ Pt/Pd = 1) after a conditioning treatment consisting of several reduction/oxidation cycles in CH₄-containing atmosphere, which has a progressively positive effect on decreasing the Pt content. Indeed, such a treatment results in a 20-fold catalytic activity enhancement for the monometallic sample (Pt/Pd = 0), whereas it has different effects on the bimetallic catalysts depending on the Pt/Pd ratio: for Pt/Pd = 0.10 the activity markedly increases up to the highest level among the tested catalysts (fresh and conditioned); for Pt/Pd = 0.25 the activity is substantially unchanged while for the Pt/Pd = 1 it is completely suppressed after the first CH₄-reducing pulse.

Such different behavior is mainly related to the influence of Pt on bulk reduction/re-oxidation properties of palladium; TPO data indicate a strong inhibition of Pt on Pd oxidation, which is completely suppressed for the Pt/Pd=1 catalyst, thus explaining the wide loss of activity after reduction for Pt/Pd=1 and confirming that PdO is the most active phase. In the case of the samples with Pt/Pd = 0.25 and Pt/Pd = 0.10 the inhibiting effect of Pt on Pd oxidation is progressively reduced, resulting in a fraction of PdO formed at the end of the conditioning process equal to 35% and 85% of total Pd, respectively.

In line with a Mars van Krevelen redox mechanism controlled by PdO surface reduction by CH₄, for the monometallic sample the activity enhancement upon conditioning is associated with an increase of bulk PdO reducibility, as determined by CH₄-TPR experiments. Such a correlation is not observed in bimetallic samples possibly due to the ability of metallic Pt to activate CH₄ under net reducing conditions (CH₄-TPR), which is suppressed under net oxidizing conditions (lean combustion).

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1. Introduction

Lean burn natural gas vehicles (NGVs) represent a promising alternative to conventional diesel and gasoline vehicles thanks to the higher H/C ratio of the fuel which results in lower CO₂ emissions, and to the reduction of many pollutants [1] in the exhausts. Nevertheless, NGVs may suffer from the emissions of unburned CH₄, a strong greenhouse gas; in this context, catalytic combustion represents a promising way to reduce CH₄ emissions from NGVs' exhausts.

In the specific conditions of the exhausts (low temperature, 300–400 °C; presence of 10–15% of H₂O; large excess of O₂, low CH₄ concentrations, 500–1000 ppm) Pd supported catalysts are widely recognized as the most active in CH₄ combustion [1–4]; nevertheless, Pd catalysts suffer from deactivation problems due to the prolonged exposure to reaction conditions containing both H₂O and S-containing compounds which are strong poisons for Pd-based systems [2–14]. Some literature reports [15–18] suggest that the addition of Pt to Pd-containing catalysts leads to an improvement of catalyst stability under reaction conditions with respect to the Pd monometallic catalyst.

However, the influence of Pt on the catalytic activity of Pd–Pt bimetallic catalysts is still a debated issue. Some authors [15,16,19,20] claim that the addition of platinum to palladium results in increasing catalytic activity while for others [17,21] the effect of Pt is not straightforward. Persson et al. [17] found that the

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activity of the fresh Pt–Pd is lower compared to the activity of the monometallic Pd samples containing the same molar amount of palladium, although upon treatment under lean reaction conditions the two systems achieve similar activity levels. Testing catalysts with constant total metal loading (2.5%, w/w) and varying amounts of Pt and Pd, Strobel et al. [21] also observed a detrimental effect of Pt on fresh catalysts prepared via flame pyrolysis. Upon temperature cycles under reaction conditions up to 1000 °C, a reverse behavior was observed, the samples with small amounts of Pt being more active than the monometallic sample. This was attributed to the ability of Pt in increasing the sintering resistance of Pd particles. On the other hand a negative effect on activity was observed at high Pt loading, although in this case the corresponding decrease of Pd load might play some role. A promoting effect of Pt on Pd dispersion was also reported by Narui et al. [16].

In our previous works on Pd/Al₂O₃ catalysts [5,22], we found a positive effect of alternated reduction/re-oxidation cycles which resulted in a marked increase of the catalytic activity of the as-prepared samples up to a high and stable level and in recovering the activity losses during prolonged operation under H₂O and S-containing atmosphere.

In this work, we investigate Pt–Pd bimetallic catalyst with different Pt/Pd atomic ratios but constant Pd loading (2%, w/w). The effect of Pt/Pd ratio on catalytic activity in CH₄ combustion was investigated in the presence of alternated reduction/re-oxidation cycles; attention was focused on the correlation between the catalytic activity evolution during the repeated cycles and the influence of platinum amount on palladium reduction–oxidation behavior.

2. Experimental

2.1. Catalysts preparation

Bimetallic Pt–Pd catalysts with constant Pd loading (2%, w/w) and different Pt/Pd atomic ratios (0, 0.10, 0.25, 1) were obtained by a dry co-impregnation technique of a commercial Al₂O₃ (Sasol Puralox SBA 140) calcined at 950 °C for 10 h (S.A. = 100 m²/g, specific pore volume 0.49 cm³/g, phase composition θ -Al₂O₃ phases with traces of γ): the procedure consists in the preparation of a water solution containing both the Pd(NO₃)₂ and the Pt(NO₃)₂ in appropriate amounts to achieve the nominal loading in a single step impregnation; a volume of the prepared solution equal to the total pore volume of the calcined alumina was then dropped on the support. The catalysts were dried at 110 °C for 2 h and calcined at 600 °C in air for 10 h.

In the following the investigated samples are identified as Pt/Pd-X, with X = 0, 0.10, 0.25, 1, accordingly to the nominal Pt/Pd atomic ratios.

2.2. Catalysts characterization

The experimental Pd and Pt loadings were determined by atomic absorption method on a Varian AA110 apparatus. XRD patterns were recorded on a Philips (PW 10507/70) powder diffractometer using a vertical goniometry and the Cu K α radiation ($\lambda_{K\alpha} = 0.1518$ nm). Specific surface areas were determined by nitrogen adsorption at 77 K using a Micromeritics Tristar apparatus according to the Brunauer–Emmet–Teller (BET) method. Metal dispersion was measured by H₂ chemisorption analysis, carried out on a Micromeritics AutoChemII instrument; the catalysts were reduced in 50 N cm³/min of H₂ in Ar at 500 °C for 1 h; after a 2 h Ar purge the temperature was decreased. 5% H₂ in Ar pulses (0.961 ml loop) were injected at regular interval time at 70 °C to avoid the problem of Pd-hydrides formation [23]. A H/Pd = 1/1 and H/Pt = 1/1 stoichiometry were assumed for H₂ chemisorption on palladium and platinum.

2.3. Catalytic activity tests

The prepared catalysts were tested in a fixed bed tubular quartz microreactor (I.D. = 7 mm) operating at atmospheric pressure, placed within an electrically heated furnace. The catalytic bed consists of 60 mg of fine catalytic powder (74–105 μ m) diluted with 60 mg of quartz powder of the same particle size. The temperature was monitored by a K-type thermocouple placed inside the catalytic bed. Composition of reactants and products at the outlet of the reactor was determined by a mass spectrometer with quadrupole detector (Balzers QMS 422) and was periodically verified through a HP6890 GC system. N₂ was used as an internal standard for gas-chromatographic analyses.

The investigated catalysts were tested according to the following experimental procedure:

Alternated lean combustion/CH₄-reducing pulses at constant temperature (350 °C): the catalysts were operated for 30 min under lean combustion conditions (0.5% CH₄, 4% O₂, 1% H₂O, 2% N₂, He at balance, 150 N cm³/min, GHSV = 150,000 Ncm³/g/h) at 350 °C; then a 30–40 s purge (He + 5% N₂) was performed to allow the desorption of species adsorbed on catalytic surface and to purge the dead volumes. After the purge the reaction atmosphere was switched to reducing conditions (0.5% CH₄, 1% H₂O, He at balance, 150 Ncm³/min, GHSV = 150,000 Ncm³/g/h) for 120 s, keeping constant the temperature at the same level. After another purge, the lean combustion conditions were finally restored. Water was added to the feed by saturation of a stream of helium, its concentration was controlled by GC and regulated through the He flow rate to the saturator to compensate for temperature and pressure variations. Argon was always fed with CH₄ and used as a tracer to clearly identify the actual switch between the lean combustion conditions or the CH₄-reducing pulse and the purge. In the following samples underwent to the multiple alternated reduction/re-oxidation cycles according to the explained procedure will be named *conditioned* catalysts while the as-prepared samples will be referred as *fresh* catalysts.

2.4. Reduction/oxidation tests

The reduction/oxidation behavior of the investigated catalysts was studied by means of the following procedures:

- (i) CH₄ temperature programmed reduction (CH₄-TPR): the catalysts were exposed to reducing atmosphere (0.5% CH₄, 1% H₂O, He at balance, 150 Ncm³/min, GHSV = 150,000 Ncm³/g/h) Gas composition at the outlet of the reactor was determined by a mass spectrometer with quadrupole detector (Balzers QMS 422) and periodically verified through a HP6890 GC system.
- (ii) Temperature programmed oxidation (TPO): four cycles of TPO were performed on a Micromeritics AutoChemII instrument, exposing the catalysts to a 2% O₂ in He atmosphere, cycling the temperature between room temperature and 900 °C.
- (iii) Oxidation under reactions conditions at constant temperature 350 °C, i.e. the same temperature of the activity test: the catalysts were exposed to lean combustion conditions (0.5% CH₄, 4% O₂, 1% H₂O, 2% N₂, He at balance, 150 Ncm³/min, GHSV = 150,000 Ncm³/g/h) for different time intervals, ranging from 0 s to 30 min; the amount of PdO formed was revealed by a CH₄-TPR (as described at point (i)) up to 350 °C, performed after a rapid quenching in inert atmosphere down to 200 °C.

Quantification of PdO was performed assuming the following stoichiometry:



Table 1

Characterization analysis results of bimetallic Pd–Pt samples.

Sample	Characterization results					$d_{\text{P}} \text{ (XRD)} \text{ (nm)}$	
	Nominal Pd amount (% w/w)	Nominal Pt/Pd atomic ratio	Composition (AAS)		$\text{H}_2 \text{ chem. dispersion (\%)}$		
			Pd and Pt loading (% w/w)	Calculated Pt/Pd atomic ratio			
2	0	Pt: 0.00 Pd: 2.14	0	21	20	PdO: 5 Pt: n.d.	
2	0.10	Pt: 0.56 Pd: 2.50	0.12	12	14	PdO: 8 Pt: n.d.	
2	0.25	Pt: 1.50 Pd: 2.50	0.33	9	8	PdO: 7 Pt: n.d.	
2	1	Pt: 4.36 Pd: 1.95	1.22	8 15 ^a	9 17 ^a	PdO: 6 Pt: 19	

^a H₂ consumption is referred only to the Pd atoms in the sample.

Formation of H₂ was used as a quantitative marker of steam reforming and WGS reactions occurring at the end of the reduction process.

3. Results and discussion

3.1. Characterization

The results of characterization analyses performed on the Pd only and on the bimetallic samples are summarized in Table 1. AAS chemical analyses of the different samples indicate that experimental Pd and Pt loadings match reasonably well with the nominal ones.

XRD spectra of the fresh samples are reported in Fig. 1. The phases were identified using the JCPDS database. For all the fresh samples, in addition to the diffraction peaks of the $\theta\text{-Al}_2\text{O}_3$ support, PdO reflections are visible in the XRD spectra while no metallic Pd is revealed. The reflections of metallic Pt were detected only in the spectrum of Pt/Pd-1, with Pt being much more crystalline than PdO as evidenced by the sharper peaks associated with metallic Pt. The fact that in the other bimetallic samples no Pt reflections were detected may be due to the low amount of platinum (<0.5%, w/w and about 1%, w/w, respectively for the Pt/Pd-0.10 and the Pt/Pd-0.25 samples); another possibility may be the formation of mixed oxides $\text{Pd}_x\text{Pt}_{1-x}\text{O}_2$ which according to a theoretical DFT study by Dianat et al. [24] were found thermodynamically stable at 1 atm of O₂ partial pressure and temperatures below 400–500 K, depending on the Pd–Pt composition. PdO crystallite size, estimated on the

basis of Scherrer's equation considering only the PdO reflections at $2\theta = 55^\circ$ and 71.9° without significant overlapping with those of the Al₂O₃ support, are in between 5 and 8 nm for each sample, suggesting that PdO crystallite size slightly increases in the presence of Pt.

Consistently with the XRD results, Pd dispersion of the monometallic system evaluated by H₂ chemisorption, is slightly higher (21%) than metal dispersions of the bimetallic samples which are in the range 8–12% (Table 1). For Pt/Pd-1, the high crystallinity of platinum evidenced by XRD, suggests that Pt might play a minor role in H₂ chemisorption; accordingly, in this specific case, the Pd dispersion has been recalculated neglecting the contribution of Pt and referring the measured number of superficial metal atoms only to number of total Pd atoms. A 15% dispersion value was obtained, which is in better agreement with the PdO crystal size evaluated from XRD, and still lower than the 20% value obtained for the monometallic sample.

The high dispersion of the monometallic catalyst may suggest that a strong interaction of palladium with the alumina support originated from the preparative procedure. In a companion study FTIR evidences, obtained comparing the spectra of the Al₂O₃ support with that of the fresh 2% Pd/Al₂O₃ sample (Pt/Pd-0 in this work) in the OH stretching region, evidenced a strong reduction in the intensity of the band associated with the basic hydroxyls of the support. This suggested that such basic hydroxyls may act as anchoring sites of the Pd(NO₃)₂ precursor, establishing strong Pd–support interactions which resist upon calcination at 600 °C. The presence of such interactions was also revealed by FTIR spectra of chemisorbed CO collected on the fresh 2% Pd/Al₂O₃ upon reduction in H₂ at 500 °C showing the features of partially ionic Pd species, likely stabilized by the support. The lower palladium dispersion values observed for the bimetallic fresh samples suggest that Pd–support interactions may be weakened in the presence of Pt.

Noteworthy, during the catalyst pre-treatment in hydrogen atmosphere up to 500 °C before chemisorption measurements, an H₂ release peak associated with Pd-hydride decomposition was observed at 70 °C for all the investigated fresh samples, which is an indication that no Pt–Pd alloy formed consistently with the co-impregnation preparation technique herein adopted [25]. Indeed Bonarowska and Karpinski [25] reported that temperature programmed palladium hydride decomposition appears as a very effective method for diagnosing the extent of alloying in Pt–Pd supported catalysts since the addition of another metal to palladium changes the propensity of the latter to form hydride in the presence of hydrogen: in particular, the preparation of a perfectly mixed Pt–Pd catalyst (alloy) should lead to a featureless H₂-TPR profile, i.e. without any H₂ peaks associated with hydrogen release during hydride decomposition. Accordingly to the different preparation procedures of Pt–Pd/SiO₂ catalysts they observed

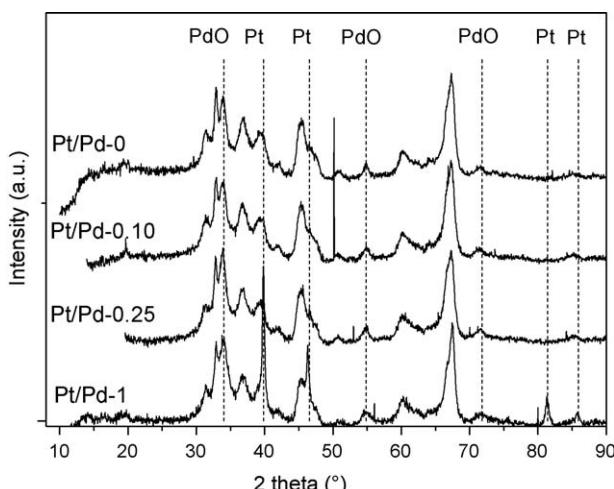


Fig. 1. XRD patterns for the fresh catalysts.

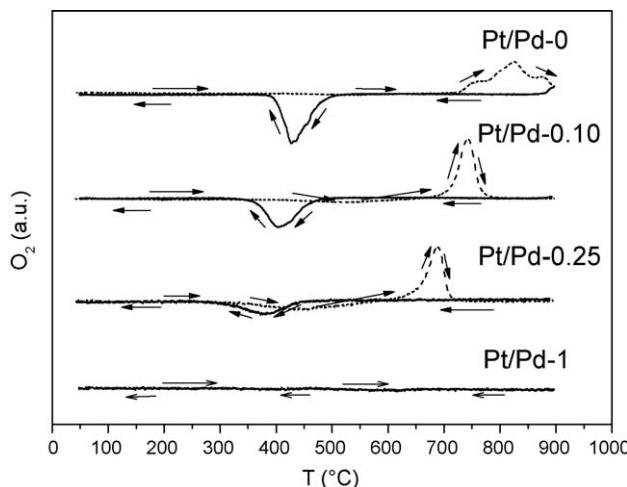


Fig. 2. O_2 evolution as a function of temperature during the third cooling ramp (solid line) and the fourth heating ramp (dash line) of the TPO test.

hydride decomposition in the case of catalysts prepared by co-impregnation technique, indicating the absence of strong interactions between Pt and Pd, while the TPR profiles of catalysts prepared by direct redox method were featureless.

3.2. Palladium redox properties of fresh and conditioned Pt-Pd catalysts

3.2.1. Reduction/oxidation under O_2 -containing atmosphere

The effect of Pt/Pd ratio on thermal reduction/re-oxidation behavior of palladium under oxygen atmosphere was investigated by means of TPO experiments. In the first heating ramp (not shown) an O_2 release peak was observed at high temperature in all the investigated samples, which quantitatively corresponds to the complete thermal decomposition of PdO . Fig. 2 shows the evolution of O_2 signal as a function of the temperature during the third cooling ramp and the fourth heating ramp of the TPO tests. For the monometallic Pd sample (Pt/Pd-0), during the cooling ramp a negative peak appears between 540 and 365 °C, associated with oxygen consumption for re-oxidation of the previously reduced palladium; during the following heating ramp, another small and broadened negative peak appears in the 365–700 °C temperature region, associated with the continuation of re-oxidation process. In the high temperature region of the heating branch, between 710 and 900 °C, the sample exhibits a complex positive peak, starting at 710 °C, associated with the thermal decomposition of PdO ; the decomposition peak presents three distinct features, centered at 755, 835 and 875 °C, possibly associated with different PdO forms, i.e. PdO in contact with metallic Pd, isolated PdO and PdO strongly interacting with the support [26].

For the Pt/Pd-0.10 and Pt/Pd-0.25 samples the O_2 profile trends are qualitatively similar to that above described; however on increasing the Pt/Pd ratio, the PdO decomposition peak, which is characterized by a single feature, shifts to progressively lower temperature, respectively 650–780 and 585–750 °C, while Pd re-oxidation during cooling requires lower thermal threshold, i.e. 526 and 500 °C, respectively. For the Pt/Pd-1 sample the O_2 signal during the TPO is completely flat; in fact, upon thermal decomposition in the first heating ramp, no re-oxidation occurs in the following cooling/heating ramps and, consequently, no further PdO decomposition is observed.

Table 2 reports the fraction of decomposed and reformed PdO during the TPO cycle of Fig. 2 for the four investigated catalysts. It can be observed that the amount of re-oxidized Pd corresponds to a

Table 2

Fraction of PdO decomposed and reformed calculated on the basis of O_2 release and consumption during the third cooling ramp and the fourth heating ramp of the TPO tests for the Pt-Pd bimetallic catalysts.

Sample	Pd re-oxidized cooling ramp	Pd re-oxidized heating ramp	Total Pd re-oxidized	PdO decomposed
Pt/Pd-0	0.89	0.06	0.95	1.08
Pt/Pd-0.10	0.62	0.12	0.73	0.76
Pt/Pd-0.25	0.25	0.28	0.53	0.46
Pt/Pd-1	0	0	0	0

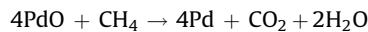
decreasing fraction of total palladium on increasing Pt/Pd ratio. The inhibiting effect of Pt on Pd re-oxidation is more evident when considering the amount of PdO formed during the cooling ramp, which markedly decreases on increasing the Pt/Pd ratio. In fact, for the monometallic Pd sample about 89% of total palladium re-oxidizes during the cooling ramp, comparing with 62% and 25% observed for the Pt/Pd-0.10 and Pt/Pd-0.25 samples, respectively. Finally, the amount of PdO decomposed decreases with Pt/Pd ratio, consistently with the lower amounts of PdO formed before thermal decomposition. Note that in the case of the Pt/Pd-0 sample, the fraction of PdO decomposed, corresponding to the 108%, is possibly affected by a higher experimental uncertain because the tail of the PdO decomposition peak is not well defined (Fig. 2).

TPO experiments clearly evidence a promoting effect of platinum on PdO thermal decomposition and an inhibiting effect on Pd re-oxidation, which are both in line with previous literature results [18,27]; in particular, our data indicate that PdO decomposition temperature progressively decreases with increasing the Pt amounts, suggesting that the presence of platinum weakens the Pd-O bond strength [18]. Upon reduction, the re-oxidation of Pd becomes progressively difficult on increasing the Pt contents, being completely hindered in the Pt/Pd-1 sample. Persson et al. [27] reported the formation of Pd-Pt alloy under reducing conditions as the possible reason for the hindered Pd re-oxidation process. They suggest that, during operation under oxidizing conditions, metallic Pd slowly dissolves out from the solid solution Pd-Pt and oxidizes to the stable PdO phase. In our case, XRD data did not provide clear indication in favour of Pt-Pd alloy formation, besides decomposition of Pd-hydride below 70 °C during the H_2 pre-treatment before the chemisorption measurements can be taken as an indication that alloying has not occurred; thus, alternative explanations such as formation of a passivating layer associated with Pt [28] should be considered to explain inhibition of Pd oxidation.

3.2.2. Reduction under CH_4 -containing atmosphere

Reducibility of the catalysts was studied by means of CH_4 -TPR; Fig. 3(a) and (b) shows the temperature evolution of CH_4 conversion during the TPR experiments for the investigated fresh (a) and conditioned (b) catalysts. In all the samples the CH_4 conversion profile first shows one or two (for the Pt/Pd-0.10 sample) peaks, associated with CO_2 and H_2O release, then a further gradual increase with temperature, in correspondence of which also CO and H_2 were detected.

Quantification of CH_4 consumption and CO_2 release during the first peaks are, for each sample, well in agreement with the following stoichiometry of PdO reduction by CH_4 :



When PdO reduction was close to completion, steam reforming and water gas shift reactions started and were responsible for the CH_4 consumption and CO and H_2 formation at higher temperature. Despite of similar general features exhibited by the investigated samples, the CH_4 -TPR profiles show marked qualitative or

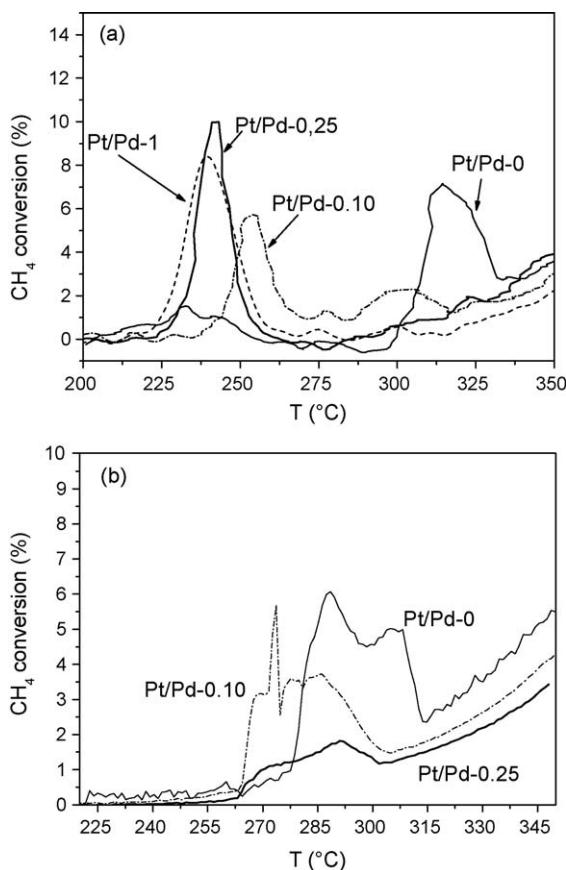


Fig. 3. Temperature evolution of CH_4 conversion during a TPR experiment on fresh (a) and conditioned (b) bimetallic Pt-Pd catalysts.

quantitative differences, depending on the Pt/Pd ratio. Over the fresh catalysts (a), reduction of PdO for the Pt/Pd-0 sample occurred with a single peak starting at 300 °C and ending at 320 °C. In the case of bimetallic samples PdO reduction is markedly anticipated; for the Pt/Pd-0.10 sample reduction starts at 235 °C and CH_4 conversion profile during TPR is characterized by the presence of two peaks, one centered at 250 °C and the other centered at 310 °C. For the Pt/Pd-0.25 catalyst, PdO reduction takes place with a single peak between 225 and 270 °C while for the Pt/Pd-1 sample PdO reduction starts at 220 °C and it is completed at 260 °C.

The CH_4 -TPR data for fresh samples clearly indicate that Pt promotes PdO reduction, as evidenced also by TPO experiments but, differently from thermal reduction which is progressively anticipated with the Pt/Pd ratio, the promoting effect is markedly appreciable already in the presence of small amounts of Pt; in fact the first reduction peak in the Pt/Pd-0.10 sample starts 65 °C below than in the Pt/Pd-0 sample, while addition of larger amounts of Pt only results in a slight further decrease of the reduction temperature, 10 and 15 °C for the Pt/Pd-0.25 and Pt/Pd-1 catalysts, respectively. Such a trend suggests that, in addition to the effect of Pt on the thermal stability of PdO, evidenced by TPO experiments, Pt can also play a role in CH_4 activation in the absence of O_2 , i.e. by dissociative adsorption of CH_4 onto the Pt metallic surface [29,30], which further promotes PdO reduction.

In the case of the Pt/Pd-0.10, the presence of two peaks at 250 and 310 °C, suggests that a fraction of PdO is easily reducible, as in the cases of Pt/Pd-0.25 and Pt/Pd-1 samples; the remaining fraction, which reduces at temperatures closed to those required by the monometallic Pt/Pd-0 catalyst, is likely associated with PdO scarcely interacting with Pt and stabilized by strong Pd–support interactions.

Fig. 3(b) shows the CH_4 conversion profile during the TPR experiments for the Pt/Pd-0, -0.10 and -0.25 conditioned catalysts; no PdO reduction peak was observed for the Pt/Pd-1 sample, indicating that no Pd^0 re-oxidation occurred after reduction by CH_4 pulses at 350 °C, in line with the results of TPO experiments. The CH_4 conversion trends are similar to those described for the fresh samples, i.e. they are characterized by a first peak, associated with PdO reduction by CH_4 according to the stoichiometry of reaction (1), followed by a gradual increase of CH_4 conversion with temperature in line with the onset of steam reforming and water gas shifts reactions. As in the case of fresh catalysts, PdO in the Pt/Pd-0 monometallic sample reduced at higher temperatures, i.e. 270–315 °C, compared to the bimetallic systems Pt/Pd-0.10 and Pt/Pd-0.25 which both reduced in the temperature range 260–300 °C, still confirming a promoting effect of Pt on PdO reducibility. The amount of CH_4 converted for PdO reduction, according to the stoichiometry of reaction (1), corresponds to the total amount of palladium present in the sample only for the Pt/Pd-0 sample while for the Pt/Pd-0.10 and Pt/Pd-0.25 ones it corresponds to 85% and 35% of total palladium, respectively, coherently with a palladium oxidation process progressively inhibited on increasing the Pt/Pd ratio.

Comparing the CH_4 -TPR of Pt/Pd-0 fresh and conditioned samples, it is evident that in the monometallic system PdO reducibility increases after the conditioning process, suggesting that a weakening of the strong metal-support interactions, which are responsible for the stronger Pd–O bond [31] of the fresh sample, occurred. Conversely, in the case of Pt/Pd-0.25, reducibility of PdO in the conditioned sample is lower compared to that of the same fresh catalyst (the onset of PdO reduction is shifted 35 °C above the value observed for the fresh catalyst). For the conditioned Pt/Pd-0.10 catalyst, the two peaks observed during the TPR profile of the fresh sample, disappear in favour of a more homogeneous situation characterized by a single peak associated to PdO with intermediate reducibility with respect to the two PdO species in the fresh catalyst.

As a whole, after conditioning PdO reducibility over Pt doped sample was much more similar to that of the monometallic Pd catalyst, suggesting that both PdO stabilization by the support and Pt promotion on PdO reducibility were weakened upon repeated reduction/re-oxidation cycles under CH_4 -containing atmospheres.

3.3. Catalytic behavior during alternated CH_4 lean combustion/ CH_4 -reducing treatment at 350 °C

3.3.1. Catalytic activity

Fig. 4 shows the time evolution of CH_4 conversion during catalysts exposure to lean combustion atmosphere at 350 °C, during several cycles of alternated CH_4 lean combustion/ CH_4 -reducing pulses. Considering the initial activity of the fresh samples (dotted lines), an increase of CH_4 conversion with the Pt/Pd ratio is evident. During repeated lean combustion/ CH_4 -reducing pulses, the catalytic activity progressively increases to a higher level compared to that of the fresh sample only in the case of Pt/Pd-0 and Pt/Pd-0.10 catalysts, which achieve a final behavior, reproducible cycle by cycle, with CH_4 conversion levels of about 70% and 80%, respectively. On the other hand for the Pt/Pd-0.25 sample the alternated pulses first result in a significant deactivation, followed by a gradual activity recovery, taking about 20 cycles to regain the initial conversion level (about 40%). Finally for the catalyst with Pt/Pd = 1 the first redox cycle results in a marked suppression of activity, which is not recovered during the following cycles.

The extent of PdO reduction during the CH_4 -reducing pulses at 350 °C (not reported), alternated to the lean combustion conditions, was evaluated by quantification, according to stoichiometry

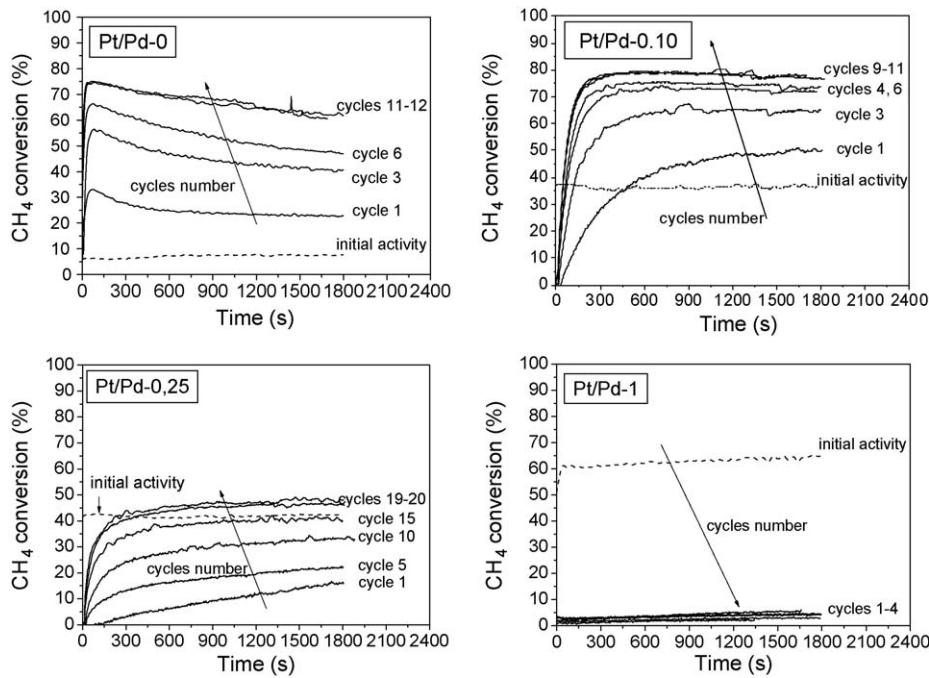


Fig. 4. Time evolution of CH₄ conversion during lean combustion conditions at 350 °C alternated to CH₄-reducing pulses at 350 °C. Dotted lines refer to catalytic initial activity and solid lines refer to activity after several alternated reduction/re-oxidation cycles.

(1), of the CO₂ peak, occurring just after the onset of reducing conditions. For all the samples the amount of PdO estimated during the first reduction pulse corresponds well to the total amount of palladium, evidencing that complete reduction has occurred, in line with CH₄-TPR results showing that PdO completely reduces below 350 °C in all the investigated samples. For the Pt/Pd-0 and -0.10 catalysts, during the successive cycles, no variation of the fraction of PdO (100% and 85%, respectively) determined in the following reducing pulses, is observed with the pulse number; on the other hand, for the Pt/Pd-0.25 sample the formed PdO decreases and then it gradually increases with the pulse number up to a value equal to 35% of total palladium. Finally for the Pt/Pd-1 sample no reduction is observed after the first cycle since no PdO is formed after the first reducing pulse.

To better evidence the activity variations of the four investigated catalysts during the conditioning process, CH₄ conversion data after 10 min exposure under lean conditions at 350 °C, verified by GC measurements, are reported in Fig. 5 as a function of

the number of redox cycles. CH₄ conversion for the fresh catalysts (cycle 0) increases with Pt/Pd ratio, in line with the CH₄ conversion trends observed in Fig. 4. During the conditioning process, CH₄ conversions markedly increase for the Pt/Pd-0 and Pt/Pd-0.10 catalysts. In the case of Pt/Pd-0.25 catalyst, CH₄ conversion markedly decreases after the first cycle and then gradually increases, achieving a final value substantially equal to the initial one. On the other hand, conversion for the Pt/Pd-1 sample markedly drops after the first cycle without any significant recovery in the following cycles.

In the case of the monometallic Pt/Pd-0 sample, TOFs of the fresh and conditioned catalyst were estimated on the basis of metal dispersion data obtained by chemisorption (Table 1) at the following conditions: $P_{CH_4} = 0.5 \text{ kPa}$, $P_{H_2O} = 1.1 \text{ kPa}$, $T = 350 \text{ °C}$; assuming an isothermal plug flow behavior of the reactor and a first order dependent on CH₄ and -1 order dependent on H₂O rate equation [32–35]. A 20-fold activity enhancement was observed at the end of the alternated redox cycles treatment, resulting in a final TOF value equal to 0.36 s^{-1} , which is comparable to the highest values reported [36] in a wide TOFs range in the literature.

A possible role of palladium dispersion variation on the activity increase with the number of cycles can be ruled out since, as shown in Table 1, palladium dispersion of Pd only sample remains unchanged before and after the redox cycles treatment. On the other hand, the observed activation with the cycle number is associated with the increased PdO reducibility by CH₄, as evidenced by comparison of CH₄-TPR profile of fresh and conditioned samples. This suggests a direct correlation between PdO reducibility and catalytic activity for a monometallic Pd catalyst in line with a Mars van Krevelen redox mechanism kinetically controlled by a surface reduction step, which is the most accepted mechanism for CH₄ combustion on PdO [22,37,38]. In a companion investigation FTIR spectroscopic evidences were collected on the effect of the conditioning treatment on Pd/Al₂O₃ catalysts with different Pd loadings. As a main evidence, FTIR investigation suggested that such activity/reducibility enhancement during the conditioning process is likely due to the weakening of Pd-support interactions, which

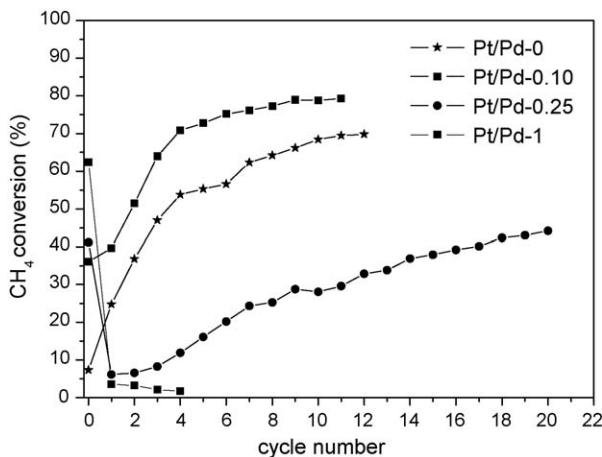


Fig. 5. CH₄ conversion under lean combustion conditions at 350 °C as a function of redox cycles number.

are likely responsible for the depressed activity level in the fresh monometallic catalyst. In fact the FTIR spectrum of the conditioned 2% (w/w) Pd/Al₂O₃ catalyst compared with those of the fresh one evidenced that the features associated to the basic hydroxyls of the alumina support, which were strongly depressed in the fresh catalysts, were similar to those observed for the pure supports. Besides the conditioning treatment resulted in the reduction of the fraction of slightly oxidized Pd^{δ+} species strongly interacting with the support, as revealed by the spectra of chemisorbed CO. Both such evidences indicated that a weakening of interactions between Pd particles and the support occurred during the conditioning process, that in turn enhanced the reducibility and activity properties of PdO particles.

The comparison of activity levels of the fresh catalysts, all containing the total amount of palladium in the form of PdO as showed by XRD and TPR analysis, evidences a promoting effect of platinum on catalytic activity, with CH₄ conversion at 350 °C progressively increasing with Pt content. Comparing this effect with the higher PdO reducibility in the presence of Pt, as revealed by CH₄-TPR and TPO experiments, may suggest again a direct correlation between catalytic performances and bulk PdO reducibility. However a closer inspection evidences that while catalytic activity is gradually promoted on increasing the Pt amount, there is an abrupt difference between reducibility of the monometallic Pd sample and the bimetallic ones, which in turn only slightly differ each other. A stronger evidence against a direct correlation between activity and PdO reducibility in Pt containing catalysts is that the fresh bimetallic samples are more reducible but less active than the conditioned Pd-only catalyst. Such lack of correlation between reducibility and activity may suggest that other steps than surface PdO reduction by CH₄ can partially control the combustion rate in bimetallic catalysts. Considering that Pt has a well evident inhibiting effect on bulk Pd re-oxidation, one can argue that Pt also hinder re-oxidation of superficial sites of PdO, thus introducing a partial rate controlling role of the re-oxidation step in the redox mechanism. To verify this explanation we performed tests over the fresh Pt/Pd-1 catalyst at different temperatures (300–375 °C) varying oxygen partial pressure (2, 4 and 8 kPa at constant CH₄ and H₂O partial pressure, respectively 0.5 and 1.1 kPa). The results evidenced that there is no effect of oxygen partial pressure on CH₄ conversion, thus ruling out the possibility of a partially controlling role of the surface re-oxidation step in the redox mechanism. Alternatively, to explain the lack of correlation between PdO reducibility and catalytic activity on bimetallic catalysts it can be suggested that Pt, which strongly promotes CH₄ dissociation in the absence of O₂ [29–30], thus resulting in the high reducibility of PdO observed in the CH₄-TPR, is poorly effective in CH₄ activation under lean conditions where the excess of O₂ can completely passivate the Pt surface [28].

Excluding a direct influence of Pt on PdO redox responsible of CH₄ combustion activity, an alternative explanation for the promoting effect of Pt on catalytic activity of fresh catalysts may consider that Pt weakens Pd-support interactions which, as discussed above, may have a detrimental effect on catalytic activity. Such decrease of Pd-support interactions in the presence of Pt is also consistent with the lower Pd dispersion obtained in the bimetallic catalysts.

The investigated bimetallic catalysts exhibit a quite different activity evolution during the conditioning process; in each case the catalytic activity variations from fresh to conditioned catalysts are not related to modifications in metal dispersion since H₂ chemisorption measurements reported in Table 1 do not show significant changes upon conditioning. In the case of Pt/Pd-1, the deactivation observed after the first reducing cycle of the conditioning process is related to the strongly inhibited Pd⁰ re-

oxidation process, which prevents PdO reformation. This confirms that PdO is the active phase under lean combustion conditions [31,39–42], Pt being only a promoter. Accordingly, studies [21,27] performed at variable Pd amounts and constant total metal loadings may bring to misleading conclusions on the effect of Pt on the intrinsic activity of PdO.

In the case of Pt/Pd-0.10 sample, the activity increase observed during the conditioning process is not correlated with an increase of PdO reducibility being the onset for PdO reduction during CH₄-TPR shifted at higher temperatures for the conditioned sample compared to the fresh one; this confirms the absence of the direct correlation between activity and reducibility in the presence of platinum and suggests that other factors may influence the catalytic activity. The situation is even more complex when considering the Pt/Pd-0.25 sample, for which a deactivation/reactivation trend is observed. The decrease of PdO amount after the first reduction pulse is likely a major responsible for the initial marked decrease of activity; during the successive cycles, the extent of palladium oxidation upon exposure to lean conditions at 350 °C increases cycle by cycle thus partly explaining the gradual increase in CH₄ conversion. However, at the end of the conditioning process only 35% of total palladium is present as PdO but the catalyst exhibits the same activity of the fresh sample, containing 100% PdO, which indicates an increase of the specific activity of PdO. As in the case of the Pt/Pd-0.10 catalyst, the higher activity of PdO after the conditioning process is not related to its reducibility, since the CH₄-TPR shows a lower reducibility of the conditioned sample compared to the fresh one. An alternative explanation for the enhancement of PdO activity after conditioning may involve the presence of a remaining fraction of palladium in the metallic form in close contact with the PdO domains, which may promote CH₄ dissociation [38–43]. Another possible reason for the intrinsic superior activity of the conditioned PdO may be the weakening of the Pd-support interaction during the conditioning process, similarly to the case of the monometallic palladium catalyst. This could be particularly the case of the Pt/Pd-0.10 sample for which poorly reducible PdO, likely stabilized by the support is evidenced in the CH₄-TPR profile of the fresh catalyst and disappears upon conditioning.

3.3.2. Reactivation/re-oxidation after catalysts conditioning

Considering the time evolution of CH₄ conversion during the consecutive lean combustion periods immediately successive to reducing pulses (Fig. 4), it is evident that in the case of the Pt/Pd-0 catalysts the CH₄ conversion during each cycle is characterized by a fast increase up to a maximum value, reached after 1–2 min, followed by a gradual deactivation; this trend is qualitatively reproduced during each cycle, with only a slight anticipation of the maximum activity with increasing the cycle number. In the case of Pt/Pd-0.10 sample, the CH₄ conversion trends does not exhibit a maximum but they are characterized by an asymptotic behavior and the time required to achieve the plateau decreases during the first four cycles and then remains constant during the successive cycles. For the Pt/Pd-0.25 sample, CH₄ conversion during each cycle is characterized by a gradual increase with time, with a reactivation dynamic becoming progressively faster cycle after cycle.

The reactivation dynamics were investigated in details over the conditioned catalysts. Fig. 6 compares the time evolution of CH₄ conversion during the 30 min of lean combustion reaction after a reducing pulse at 350 °C, for the stabilized Pt/Pd-0, -0.10 and -0.25 samples. In the monometallic Pt/Pd-0 sample the CH₄ conversion increases and reaches its maximum value after about 100 s, then it slowly decreases. In the cases of the bimetallic samples the dynamics of reactivation are progressively slower with increasing the Pt amount: Pt/Pd-0.10 reaches a plateau after about 400 s

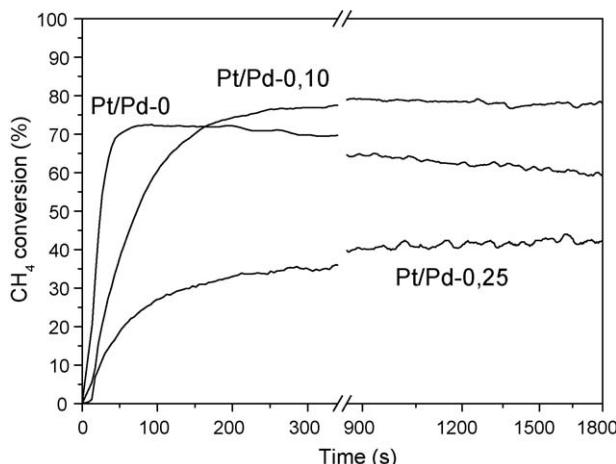


Fig. 6. Time evolution of CH_4 conversion during CH_4 lean combustion conditions after a reducing pulse at 350 °C.

whereas in Pt/Pd-0.25 the CH_4 conversion continuously increases during the 30 min lean combustion phase.

Fig. 7 shows the extent of palladium oxidation (X_{PdO}) as a function of time exposure to the CH_4 lean combustion atmosphere at 350 °C for the catalysts with $\text{Pt}/\text{Pd} \leq 0.25$; X_{PdO} was defined as the ratio of the amount of reducible PdO , as determined by CH_4 -TPR upon rapid quenching of the samples after exposure to reaction mixture for a given period, to the total amount of palladium in the catalyst. For the Pt/Pd-0 sample, the extent of palladium oxidation gradually increases with time, reaching about 90% in 120 s and being then slowly completed in about 30 min; the bimetallic Pt/Pd-0.10 and Pt/Pd-0.25 samples exhibit the same increasing trend but the oxidation process is progressively slower with increasing the Pt/Pd ratio: for the Pt/Pd-0.10 sample, 60% of PdO is formed upon 150 s and a maximum of 85% is reached after 30 min; for the Pt/Pd-0.25 sample, less than 20% PdO is formed upon 150 s and only 35% PdO is obtained after 30 min.

Comparison of data in Figs. 6 and 7 clearly shows a strong correlation between reactivation and re-oxidation dynamics under lean conditions, which is consistent with the assumption that the marked increase of catalytic activity is associated with the formation of PdO by re-oxidation of inactive metallic Pd. Along similar lines, the acceleration of the reactivation dynamics with the increasing cycles number observed in Fig. 4, is likely related to a Pd re-oxidation process becoming faster cycle by cycle. Additionally it is evident that the slower reactivation dynamic of the bimetallic

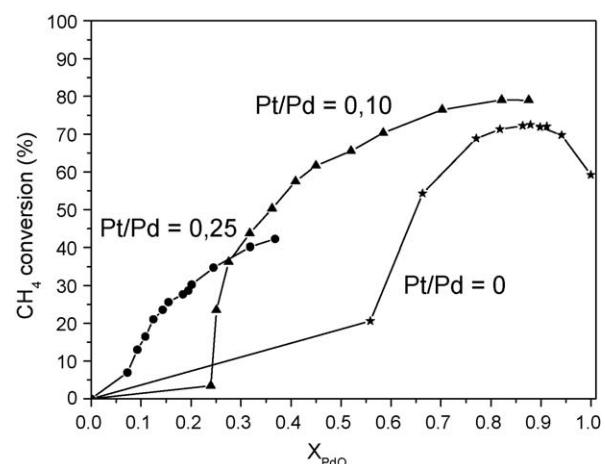


Fig. 8. CH_4 conversion during lean combustion conditions at 350 °C as a function of the extent of PdO reformation.

catalysts compared to the monometallic one is due to the inhibiting effect of Pt on palladium re-oxidation process at 350 °C.

To better focus the correlation between PdO formation and activation, Fig. 8 reports the trend of CH_4 conversion at 350 °C versus the corresponding extent of palladium oxidation evaluated after different exposure times to lean combustion atmosphere. A general correlation is still evident but significant deviations clearly emerge from this close comparison. In the early stage of the process (15–30 s corresponding to the first two points of each curve) the activity is markedly lower than expected from the corresponding amount of PdO . This is possibly due to the fact that 15–30 s exposure to lean combustion atmosphere are enough to allow a significant O_2 uptake, e.g. via O diffusion in bulk palladium crystallites [44], especially in the monometallic Pd sample and to a less extent in the Pt/Pd-0.10 sample, but does not allow reconstruction of the active bulk PdO . Noteworthy, accordingly to the experimental procedure herein adopted, such reconstruction may occur during the heating ramp of the CH_4 -TPR before the reduction peak is finally detected, i.e. below the threshold temperature of CH_4 activation as a reducing agent.

The Pd only sample also shows a reverse trend, with CH_4 combustion activity which decreases with the extent of the oxidation process for fraction of PdO above 90%. In a previous investigation [22] a possible role of H_2O poisoning was invoked to explain such a trend, as an alternative to the hypothesis that Pd-PdO mixture performs better than pure PdO [38,43]. However the behavior of Pt/Pd-0.10, which does not exhibit such a reverse trend while reaching a maximum fraction of PdO of 85%, provides an evidence in favour of the promoting effect of small amounts of metallic Pd on the CH_4 combustion activity.

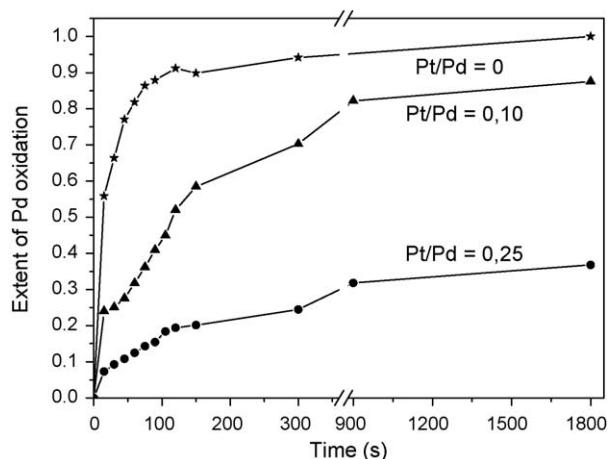


Fig. 7. Extent of metal Pd re-oxidation during lean combustion reaction in function of time lengths of exposure to lean combustion atmosphere at 350 °C.

4. Conclusions

The results obtained in this work on CH_4 combustion activity and reduction/re-oxidation behavior of bimetallic $\text{Pd-Pt/Al}_2\text{O}_3$ catalysts with constant Pd loading (2%, w/w) and different Pt/Pd atomic ratios (0, 0.10, 0.25 and 1) pointed out the following main conclusions:

- (1) Addition of Pt progressively promotes thermal decomposition and chemical reduction (by CH_4) of PdO . On increasing the Pt/Pd ratio oxidation of metallic Pd is also progressively inhibited, being completely hindered for the Pt/Pd-1 sample.
- (2) Repeated Pd reduction/re-oxidation cycles are effective in increasing catalytic activity of Pt/Pd-0 and Pt/Pd-0.10 samples: these systems exhibit a marked activation during the

conditioning process up to the highest levels among the catalysts tested in this work. Reduction/re-oxidation cycles are also beneficial for the specific activity of PdO in Pt/Pd-0.25, but overall catalytic performances of this system are limited by the extent of PdO formation under the investigated conditions. Complete suppression of PdO formation is also responsible for the marked deactivation of Pt/Pd-1 upon reduction, proving that PdO is the active phase in CH₄ combustion since when absent CH₄ conversion is negligible.

(3) Pt inhibiting effect on palladium re-oxidation also affects reactivation dynamics, which is progressively slower the higher is the Pt/Pd ratio. This may have negative practical consequences when periodical reduction would be applied for catalyst regeneration. In fact the longer period required to achieve high conversion performances would result in higher CH₄ emissions in the overall working cycle.

(4) The correlation of PdO reducibility to CH₄ combustion activity which is observed in monometallic catalyst, in line with a redox mechanism kinetically controlled by the reduction step, does not apply in the case of bimetallic samples. Such lack of correlation is possibly due to the different abilities of Pt to activate CH₄, which is effective onto the metallic surface which prevails in the absence of oxygen (CH₄-TPR) and poor onto the passivated surface which occur in the presence of excess of oxygen (lean combustion).

(5) As a whole, the effect of Pt on PdO CH₄ combustion activity is not straightforward. Depending on several factors, such as the extent of PdO formation, the strength of Pd-support interactions, the stabilization of metallic Pd, Pt may act as an inhibitor or a promoter of catalytic activity.

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